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Preliminary communication

INSERTION OF ACETYLENE INTO OSMIUM—HYDROGEN BONDS IN CLUSTER COMPLEXES

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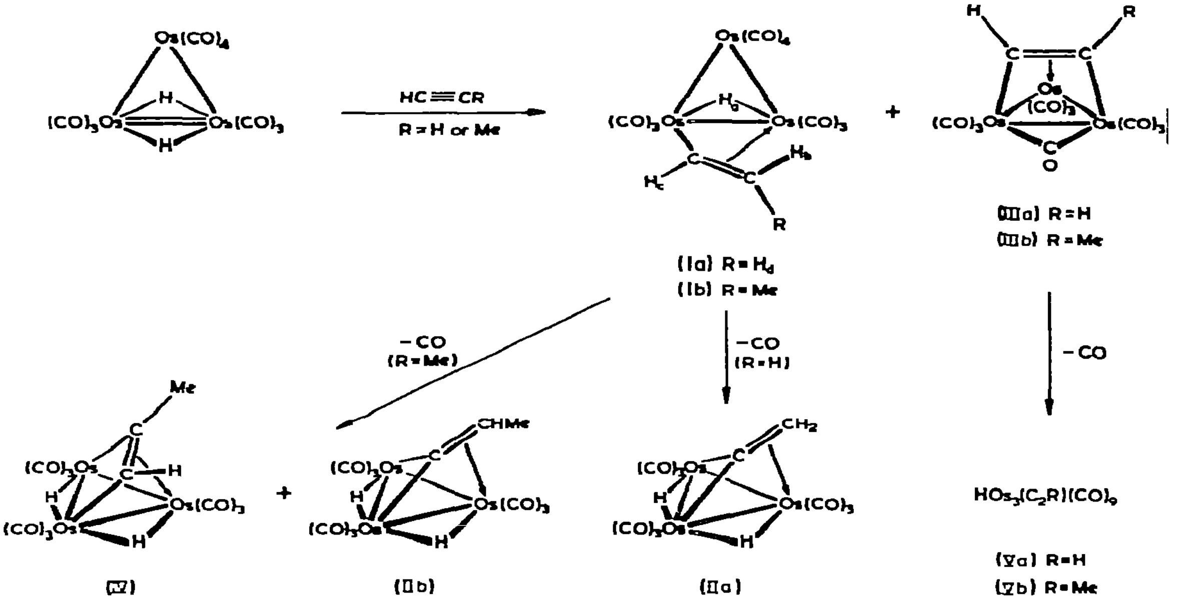
Summary

Complex $H_2Os_3(CO)_{10}$ reacts with acetylene or methyl-substituted acetylenes to give complexes of type $HOs_3(CH{=}CHR)(CO)_{10}$ (R = H or Me) and $Os_3(R_1C_2R_2)(CO)_{10}$ (R_1 and R_2 are H or Me) which convert to nonacarbonyl complexes with hydrogen transfer from ligand to metal.

The hydrogen ligands in the complex $H_2Os_3(CO)_{10}$ bridge two osmium atoms linked by what is believed to be a double osmium—osmium bond on the basis of the EAN rule, bond lengths and qualitative MO arguments [1]. In examining whether or not the reactivity of the complex relates to this apparent unsaturation, we have found that $H_2Os_3(CO)_{10}$ readily reacts with acetylene (1 atm) in hexane at room temperature (24 h) to give $HOs_3(CH{=}CH_2)(CO)_{10}$ (Ia) in excellent yields. The spread of chemical shifts for the C_2H_3 group in the ^1H NMR spectrum [H_a, τ 29.38; H_b, τ 6.60; H_c, τ 2.42; H_d, τ 5.02; J_{bc} 14.9, J_{cd} 9.7, J_{bd} 2.2, J_{ac} 1.7, J_{ad} 2.2 and J_{ab} ~ 0 Hz; $CDCl_3$] indicates a bridging 3*e*-donating ligand as shown in Scheme 1. Thus all Os—Os bonds in Ia are single and no further reaction with acetylene occurs at room temperature. It appears from this that it is the double metal—metal bond in $H_2Os_3(CO)_{10}$ that allows the ready addition of acetylene. The dihydrido complex may be regenerated by reaction of H_2 with Ia and reaction with CO gives $Os_3(CO)_{12}$ very readily.

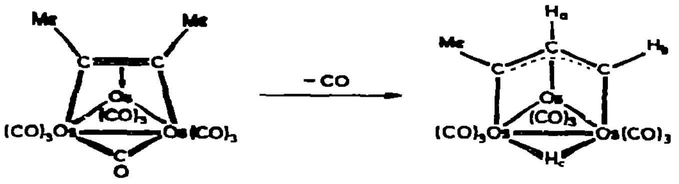
We had proposed [2,4] prior to its isolation that complex Ia is an intermediate in the double oxidative addition of ethylene to $Os_3(CO)_{12}$ in refluxing octane to give $H_2Os_3(CCH_2)(CO)_9$ (IIa) [2-4] and indeed, in refluxing octane, complex Ia rapidly converts to IIa (70%) and $Os_3(CO)_{12}$ (30%). Carbon monoxide loss with hydrogen transfer from ligand to metal is a characteristic reaction of organometallic triosmium clusters recently to become apparent. In this work we have established that the ligand CCH_2 may be derived either from acetylene or ethylene.



Scheme 1

Further reaction of Ia with acetylene in refluxing hexane gives a complex mixture containing some $Os_3(C_2H_2)(CO)_{10}$ (IIIa). With methyl-substituted acetylenes this subsequent reaction occurs more readily. Thus propyne with $H_2Os_3(CO)_{10}$ at room temperature gives complexes $HOs_3(CH{=}CHMe)(CO)_{10}$ (Ib) and $Os_3(HC{\equiv}CMe)(CO)_{10}$ (IIIb), whereas 2-butyne gives $Os_3(MeC{\equiv}CMe)(CO)_{10}$ (IIIc) and we did not detect the analogue of Ia and Ib. The *cis*-addition of Os—H across propyne to form Ib was established from its ^{1}H NMR spectrum; $J(H_b{-}H_c)$ = 13.5 Hz. Complex Ib loses CO in refluxing octane to give an inseparable mixture of IIb and IV, a similar mixture to that obtained in the direct reaction of propene with $Os_3(CO)_{12}$ [4]. This indicates that the extent of 1,1- versus 1,2-substitution of olefins on reaction with $Os_3(CO)_{12}$ is determined in the second oxidative addition step.

Complexes IIIa-IIIc are exceptional for osmium in having bridging carbonyl groups [ν(CO) ~ 1850 cm^{-1}]. This and the symmetrical nature of the acetylene fragment for IIIa and IIIc supports the structure shown. Complexes III, like complexes I , all show hydrogen transfer from ligand to metal. Thus complexes IIIa and IIIb, derived from terminal acetylenes, readily lose CO in refluxing hydrocarbons to give the acetylido species $HOs_3(C_2R)(CO)_9$, complexes Va and Vb, analogous complexes of which are known for ruthenium [5] and a structure has been established [6]. The 2-butyne derivative IIIc must behave differently, yet converts to a comparable monohydride $HOs_3(C_4H_5)(CO)_9$ (VI) in refluxing heptane (Scheme 2). Like the acetylide ligands in V, the C_4H_5 ligand must be a 5e-donor and we believe it has the structure given. The IR spectrum around 2000 cm^{-1} (2099m, 2070vs, 2046vs, 2025vs, 2017m, 2000s, 1992m, 1986m, 1978m; C_6H_{12}) is very similar to those of related ruthenium complexes (for examples, see refs. 7-9) and its ^{1}H



(IIIc) (XI)

Scheme 2

NMR spectrum [H$_a$, τ 5.78; Me, τ 7.25; H$_b$, τ 7.52; H$_c$, τ 32.23; all singlets, $CDCl_3$ solution] shows very different shifts to that of $HRu_3(C_4H_5)(CO)_9$ [7] so the C_4H_5 group may be differently bound.

Acknowledgement

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